

Mechanistic Investigation of the Rechargeable Li-Sulfur Batteries

U.S. DEPARTMENT OF

ENERGY

Energy Efficiency & Renewable Energy

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Objective: Fundamental research on the mechanism of the “shuttle effect” inhibition for the rechargeable Li-S batteries; development of the electrode and the electrolyte systems which can mitigate the “shuttle effect” so the low self-discharge and long cycle life can be achieved.

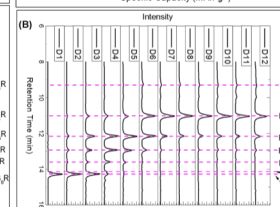
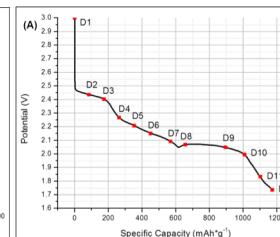
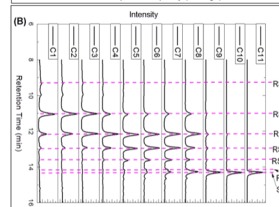
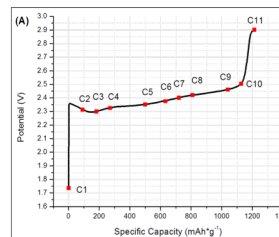
Impact:

- With the unique *in-situ* electrochemical-HPLC/MS technique developed in this program, the mechanisms of all the reactions in a Li-S cell can be revealed.
- The interactions between additives and the soluble polysulfides can be investigated real-time toward mitigation of “shuttle effect”.
- The results of the project will guide the development of sulfur cathode and Li-S designs for electric vehicles.

Accomplishments:

- *In-situ* electrochemical-HPLC/MS/UV system was developed to identify polysulfide ions real time during the cell operation of a Li-S cell.
- *In-situ* electrochemical-laser confocal microscopic cell was made to investigate the surface of Li anode during the cycle of Li-S cell. The Li surface morphology change can be observed in real time.
- By means of the *in-situ* methods, the distribution of dissolved polysulfide ions can be monitored real time during the discharge and recharge of a Li-S battery.
- The chemical equilibriums of the dissolved polysulfide ions were determined, so did the sulfur redox reaction mechanism.

Title of Graph: The mechanism of the sulfur redox reaction was proposed by the determination of every polysulfide ions at different stage of the redox reaction



>2.3 V, first plateau, major species are bold
 $S_8 \xrightarrow{ne} (S_8^{2-} + S_7^{2-} + S_6^{2-} + S_5^{2-} + S_4^{2-} + S_3^{2-})$
 $S_8^{2-} \rightleftharpoons S_6^{2-} \rightleftharpoons S_4^{2-}$
 Between 2.3 and 2.1 V, major species are bold
 $S_8^{2-} + S_7^{2-} + S_6^{2-} + S_5^{2-} \xrightarrow{ne} S_4^{2-} + S_3^{2-} + Li_2S_2 \downarrow + Li_2S \downarrow$
 <2.1 plateau, major species are bold
 $S_5^{2-} + S_4^{2-} + S_3^{2-} \xrightarrow{ne} Li_2S_2 \downarrow + Li_2S \downarrow$
 $S_5^{2-} \rightleftharpoons S_4^{2-} \rightleftharpoons S_3^{2-}$

Cathode potential <2.4 V
 $Li_2S_2 \downarrow + Li_2S \xrightarrow{ne} S_8^{2-} + S_7^{2-} + S_6^{2-} + S_5^{2-}$
 $S_8^{2-} \rightleftharpoons S_7^{2-} \rightleftharpoons S_6^{2-} \rightleftharpoons S_5^{2-}$
Cathode potential >2.4 V
 $S_8^{2-} + S_7^{2-} + S_6^{2-} + S_5^{2-} + S_4^{2-} + S_3^{2-} \xrightarrow{ne} S_8$
 $S_8^{2-} \rightleftharpoons S_7^{2-} \rightleftharpoons S_6^{2-} \rightleftharpoons S_5^{2-}$

FY 18 Milestones:

- Q1: Determination of the reactions between polysulfides and the materials in a Li-S cell during the storage, thus the stability of battery components.
- Q2: Tabulating the list of potential inhibitive additives to mitigate “shuttle effect”; start the tests and understanding the mechanism of such effects.
- Q3: Complete testing the inhibitive additives; start to explore and design sulfur containing electrode materials..
- Q4: Complete the preliminary engineering design and test for the new sulfur containing electrode materials.

FY18 Deliverables: Quarterly Reports and the results for the additives to mitigate “shuttle effect”.

Funding:

— FY18: \$300,000, FY17: \$300,000, FY16: \$300,000

OVERCOMING INTERFACIAL IMPEDANCE IN SOLID-STATE BATTERIES

U.S. DEPARTMENT OF

ENERGY

Energy Efficiency &
Renewable Energy

PI/Co-PI: Eric Wachsman (UMD)/ Liangbing Hu (UMD) / Yifei Mo (UMD)

Objective: Develop a multifaceted and integrated (experimental and computational) approach to reduce interfacial impedance of garnet-based solid-state Li ion batteries (SSLiBs).

Impact:

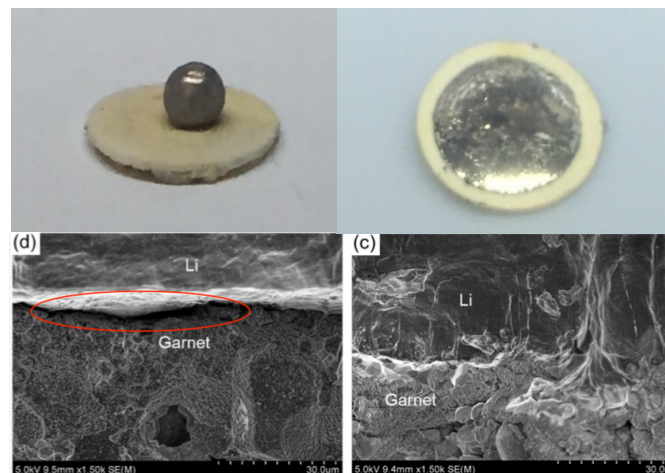
- Overcome primary issue with garnet electrolyte SSLiBs, interfacial impedance, thus enabling an entirely new safer (non-flammable) battery platform
- Enable highest capacity Li-metal anodes with no dendrites for higher energy density batteries (~500 Wh/kg)

Accomplishments: (FY16)

- First comprehensive investigation of interface impedance in garnet based SSLiBs
- Determined interfacial impedance as function of electrolyte/electrode contact area in 3D controlled solid state structures
- Developed computational models to investigate interfacial ion transport with interlayers
- Developed multiple efficient interlayer solutions to decrease interfacial impedance
- Demonstrated low interfacial impedance ($\sim 10 \Omega \text{ cm}^2$) between both electrolyte and Li-metal anode and between electrolyte and cathode

EXAMPLE

Li Metal Wetting of Solid-State Electrolyte



Developed surface treatment to allow Li-metal wetting thus dramatically reducing interfacial impedance

FY 17 Milestones:

- Demonstrate full cells with NMC cathode
- Demonstrate full cells with Sulfur cathode
- Develop models to investigate interfacial transport for Li-S and Li-NMC SSLiBs
- Achieve full cell (Li-S or Li-NMC) performance of 350-450 Wh/kg and 200 cycles

FY17 Deliverables: Submission of 12 improved cells for government testing and evaluation

Funding:

— FY17: \$401,634, FY16: \$401,635 FY15: \$409,608